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THE VAPOR PRESSURE OF SALT - HCL - WATER SOLUTIONS
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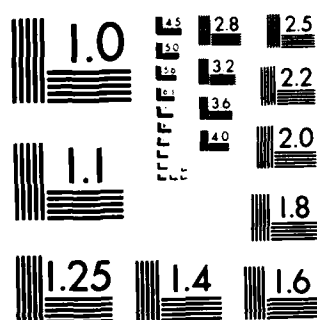
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ADA 127765

January 1983

Interim Report: Covering Period 1 Dec 81 to 30 Nov 82

THE VAPOR PRESSURE OF SALT -- HCl --WATER SOLUTIONS BELOW 0C

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 83-0347	2. GOVT ACCESSION NO. AD-A127 765	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE VAPOR PRESSURE OF SALT-HCl-WATER SOLUTIONS BELOW 0C		5. TYPE OF REPORT & PERIOD COVERED INTERIM 1 Dec 81 - 30 Nov 82
7. AUTHOR(s) Eugene Miller		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS UNIVERSITY OF NEVADA RENO MACKAY SCHOOL OF MINES RENO, NV 89557		8. CONTRACT OR GRANT NUMBER(s) AFOSR 77-3333
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA Bolling AFB, D.C. 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2308/A1 61102F
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE Jan 83
		13. NUMBER OF PAGES 8 plus 23 figures
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) THERMOCHEMISTRY, VAPOR PRESSURE, SOLUBILITY, NaCl-HYDROCHLORIC ACID		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Vapor-liquid equilibria data are presented for NaCl-HCl-water solutions, HCl mol fraction from 0.03 to 0.22, solution temperatures between 0 and -40C, and NaCl molalities from 0. to near saturation. The system exhibits a minimum boil- ing pressure with acid composition, similar to the behavior of a pure acid sol- ution. The vapor composition variation with liquid composition is much more complex because of the additional degree of freedom of the three-component sys- tem. The measurements for this system are completed.		

ABSTRACT

Vapor - liquid equilibria data for NaCl-HCl-water solutions, HCl mol fraction from 0.03 to 0.22, solution temperatures between 0 and -40C, and NaCl molalities ranging from 0 to near saturation are presented. The system exhibits a minimum boiling pressure with acid concentration, similar to the behavior of a pure hydrochloric acid solution. However, the vapor composition variation with liquid composition is much more complex because of the additional degree of freedom of the three-component system. The partial pressure of water in equilibrium with the solutions is depressed by the dissolved NaCl at all acid concentrations. The partial pressure of HCl over the salted solutions is higher than for the corresponding pure HCl solution at high salt concentrations and low acid concentrations below a salt-free HCl mol fraction of 0.18. The measurements for the NaCl-HCl-water system are completed, those for CaCl₂-HCl-water continuing, and the brief evaluation of the KCl-HCl-water system planned. A previous conclusion that a solid NaCl hydrate forms in equilibrium with the saturated acid solution below 0C appears to be incorrect.

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INTRODUCTION

The vapor pressures of hydrochloric acid solutions are important to the modelling of secondary smoke in reduced smoke ammonium perchlorate solid propellant rocket plumes, ref 1, since the growth of secondary smoke droplets is dependent on their equilibrium behavior. In addition, the nature of strong electrolytes in aqueous solution is of fundamental interest. No data were available for pure hydrochloric acid below 0C prior to the measurements made by the principal investigator at the University of Nevada, ref 2, under the sponsorship of AFOSR. The experimental effort since has been directed toward hydrochloric acid solutions containing dissolved sodium chloride or calcium chloride. The studies of the solutions containing sodium chloride have been completed and are reported in the present Interim Report. Studies of the calcium chloride solutions are continuing.

Inorganic salts dissolved in hydrochloric acid will significantly modify its equilibrium behavior due to their effects on the activities of the HCl and water in the liquid phase, ref 3. The change in the vapor pressure alters the formation of secondary smoke, refs 4, 5. The major contaminants found in ammonium perchlorate are sodium and potassium salts. Tricalcium phosphate added to ammonium perchlorate for ease in processing provides a major source of soluble electrolyte. All of these cations are finally found in the rocket plume in sufficient quantity to nucleate the secondary smoke droplets and to subsequently dissolve and influence the dynamics and nature of the smoke. Typically there are approximately 0.2 wt.pct. of tricalcium phosphate and 200 ppm of sodium cation in the ammonium perchlorate. Assuming that the average condensation nucleus radius is 0.06 micron, ref. 6, the number of nuclei emitted from a typical reduced smoke rocket nozzle as calcium chloride is estimated to be 3.6 ± 15 per sec per sq ft and 1.2 ± 13 per sec per sq ft as NaCl. Ref 1 reported 8.4 ± 14 per sec per sq ft measured for such a reduced smoke rocket. There is clearly sufficient salt present in the rocket plume to nucleate the observed secondary smoke. Inclusion of additional soluble salt by entrainment by the plume from the atmosphere is relatively small. More important are soluble salts derived from ballistic modifiers and combustion resonance suppressors added

to propellant formulations. If iron and copper modifiers are avoided, none of the others commonly added will produce salts soluble enough to effect significant changes in the behavior of the hydrochloric acid droplets. The original choices of NaCl_2 and CaCl_2 as the salts for the study were based on these practical considerations as well as for their scientific interest because of their differences in ionic strength. A very limited consideration of KCl has subsequently been added for the current contract period.

Data are available in the literature for the activities of $\text{NaCl-HCl-H}_2\text{O}$ solutions for 0 to 50°C , ref 3, permitting the prediction of vapor pressure for this temperature range. The present study covers the nominal range from 0 to -40°C . Less data exist for $\text{CaCl}_2\text{-HCl-H}_2\text{O}$ above 0°C but only the 0 to -40°C range is being studied since this is more important from a smoke viewpoint. Further, the experimental equipment is most suitable for the latter range.

EXPERIMENTAL

As shown schematically in Figure 1, a 2 liter Pyrex flask is immersed in a methylene chloride bath cooled by a two-stage mechanical refrigeration system. The temperature of the bath is maintained within $\pm 0.1^\circ\text{C}$, monitored by a calibrated platinum resistance thermometer. Removal of air from the system is accomplished by a mechanical vacuum pump in series with a liquid nitrogen trap. Pressures are measured with two MKS Baratron Type 220 gauges ($1-04$ to 1 torr, and $1-02$ to $1+02$ torr) calibrated by the manufacturer by means of a CEC air deadweight tester and a transfer standard to ± 0.02 pct of full range. The acid is distilled away from the salt in a closed glass system. Samples of the distilled acid and the salt dissolved in water are analyzed to $\pm 2\%$ max. standard deviation using a Barnstead Model PM-70CB electroconductivity bridge, a Yellowstone YSI 3400 Pyrex cell and standard solutions.

Vapor compositions are measured for samples drawn from the vapor chamber into a Varian VGA-100 quadrupole mass filter. The ratio of partial pressures of water to HCl is determined from the recorded mass spectra in the range of 14 - 20 and 34 - 40 mass numbers. The spectra are obtained at mass filter pressures of approximately $3.-06$ torr, sampling continuously from the

vapor chamber which is open to the solution flask, and pumping on the mass filter with a Varian 20 liter per sec Vacuon pump. As described in ref 2, the relative sensitivity of the instrument to water and HCl was calibrated as a function of composition.

All valves and fittings are made of AISI 304 and 315 stainless steel. Viton O-rings and copper gaskets are used in the valves and fittings. All metal parts in continuous contact with the acid vapors are coated with Dow vacuum grease. No significant corrosion of metal parts from the vapors has been experienced.

The experimental procedure used is as follows:

(1) The solution is cooled to the desired temperature overnight or longer. The whole system is then pumped down to a pressure below the range of the Baratron gauges. The solution itself is deaerated by slowly opening the flask to the evacuated vapor chamber, allowing the system to reach equilibrium, re-isolating the flask and re-evacuating the vapor chamber - repeating the cycle at least five times before taking any data.

(2) The flask valve is opened slowly to the evacuated vapor chamber to avoid violent boiling and splattering, and the pressure measured as a function of time over at least a 16 min period. Measurements are repeated usually five or more times. Small corrections for minor leaks and adsorbed gases in the vapor chamber are derived from the slope of the vapor pressure - time curve.

(3) Subsequently, mass filter analyses are made by bleeding samples of gas from the vapor chamber into the gas analyzer. Measurements are made at intervals until equilibrium is established, usually after two hours. Small corrections are made for background water and HCl in the gas analyzer. The mass filter is pumped down below 1×10^{-8} torr before introducing the gas sample in order to minimize the background.

(4) A sample of the liquid solution is taken as required and the acid separated from the salt by distillation. Acid samples are diluted by 50 to 200 to 1, depending on the initial concentration. The salt recovered is dissolved in 20 ml of distilled water and generally is not diluted further. The conductivity of the acid samples is compared with those of certified N/30 and N/10 standards. Salt solution conductivity is compared with standardized 0.0025, 0.005, 0.04, and 0.1N solutions made up from reagent grade salt and distilled water.

RESULTS

I. Solid NaCl Hydrate.

It was previously reported, ref 7, that solubility data for NaCl in hydrochloric acid supported the formation of a solid hydrate in equilibrium with the saturated acid solution below 0°C. Solubility studies conducted during the present period indicate that the appearance of a maximum in solubility below 0°C was more likely due to solubility kinetic factors. Some of the data suggest that the formation of the solid hydrate may be real, but the experimental effort required to establish its presence is outside the scope of the present study. If time permits, the subject will be pursued further.

II. Total Pressure

The total pressure over a NaCl-HCl-H₂O solution is presented as a function of salt-free mol fraction of HCl, XHCl, salt molality, m , and solution temperature, T , in Figure 2. The plot covers the range of salt molalities from 0, pure acid, to intermediate and "saturated" concentrations. The "saturated" solutions are near but not at saturation in general because of the kinetic factors mentioned above. An expanded scale for each of the pure acid solutions studied is given in Figures 2(a) through 2(f).

III. Partial Pressure HCl

Presentation of all the data on a single plot is too complex. Instead, in Figure 3 (a) through (d) there is plotted the ratio of the partial pressure HCl of the salted solution, p' , to that of the pure solution, p , as a function of NaCl molality, m , with XHCl and temperature, T , as parameters. Plots of the partial pressures of HCl for each XHCl as a function of T and m are given in Figure 4(a) through (e). "Saturated" molalities are near saturation as noted above.

IV. Partial Pressure H₂O

Partial pressures H₂O for each XHCl as a function of T and m are displayed in Figure 5(a) through (f). Again a single plot for all the data was avoided. Molalities labelled as "saturated" are near saturation as described above.

DISCUSSION

I. Total Pressure

The total pressures observed are independent of molality for a given acid concentration except for the highest acid concentrations, X_{HCl} of 0.2227 and 0.1831, and the lowest acid concentration studied, $X_{HCl} = 0.0361$. For $X_{HCl} = 0.1831$, the curve for the intermediate molality appears to be somewhat higher than for the pure acid. Actually the difference seen is due to the use of an average concentration of pure acid for the plot since the solutions varied from each other slightly in concentration. Near saturation solutions for the highest and lowest acid concentrations were lower than for pure acid.

The NaCl-HCl-H₂O system exhibits generally the same minimum pressure characteristic as pure HCl-H₂O, indicative of an azeotrope, but much in a much more complicated fashion since the three component solution has an additional degree of freedom. The closer the system is to the minimum total pressure conditions, the more the total pressure is independent of acid concentration and molality. As will be discussed below this is not true for the partial pressure behavior, particularly for HCl.

II. Partial Pressure HCl

A priori, it would be expected that the addition of a common ion, Cl⁻, would result in a general increase in partial pressure of HCl. Experimentally it is found that for the hydrochloric acid system it is only true for dilute solutions of acid at low molalities, i.e. $X_{HCl} = 0.0713$ or less and m below 1. At the highest mol fractions of HCl, greater than 0.1831, the HCl partial pressure of the salted solution is always lower than for the pure acid. At intermediate acid concentrations, $X_{HCl} = 0.1464$ to 0.1107, the partial pressure decreases initially with salt molality before increasing. At the lower HCl mol fractions, X_{HCl} of 0.0713 and 0.0361, the partial pressure reaches a maximum with molality. Also at lower acid concentration, the ratio of the partial pressures of salted to pure solutions appears to be independent of temperature. This is not true at higher acid concentrations. The complex behavior of the system is also apparent from an examination of the individual plots for each acid mol fraction given in Figure 4. Again it was necessary to use the average acid concentration in the latter figures. Actual pure acid concentration partial pressures were used for the p'/p plots

for each salted solution in the Figure 3 plots.

It had initially been expected that the Setschenow equation,

$$p^*/p = y^*P^*/yP = \exp(km)$$

as exemplified by the Figure 3 plots would yield a linear plot of p^*/p with m . Although the representation of the data by such a plot is convenient, clearly the salt coefficient k is not independent of m . The equation cannot therefore be used to test rigorously the consistency of the experimental data.

III. Partial Pressure H₂O

Except for perhaps the highest mol fraction HCl, XHCl of 0.2227, as expected the partial pressure of H₂O of the salted solutions was lower than for the pure acid solution. The higher partial pressure for the concentrated solution is unlikely. The apparent increase is likely due to the limits in sensitivity of the mass filter and to problems in interpolating the pure acid data in this acid concentration range due to the steep gradient of the curve.

IV. General

The complexity of the behavior of the NaCl-HCl-H₂O system demonstrated by the experimental results clearly indicates how futile it is to try to predict the vapor pressures from existing electrochemical data for temperatures above 0°C. In attempting to predict the behavior of the KCl-HCl-H₂O system from the limited data to be obtained, this should be kept in mind.

FUTURE PLANS

(1) Complete the measurement of the equilibrium vapor pressures of the CaCl₂-HCl-H₂O solutions for CaCl₂ concentrations between zero molality and saturation for nominal acid concentrations of 0.03 to 0.22 mol fraction and at temperatures between 0 and -40°C.

(2) Perform thermodynamic consistency tests on the salt-acid solution data. Repeat measurements as required.

(3) Complete the manuscript for the NaCl-HCl-H₂O vapor-liquid equilibria data for publication in an archive journal.

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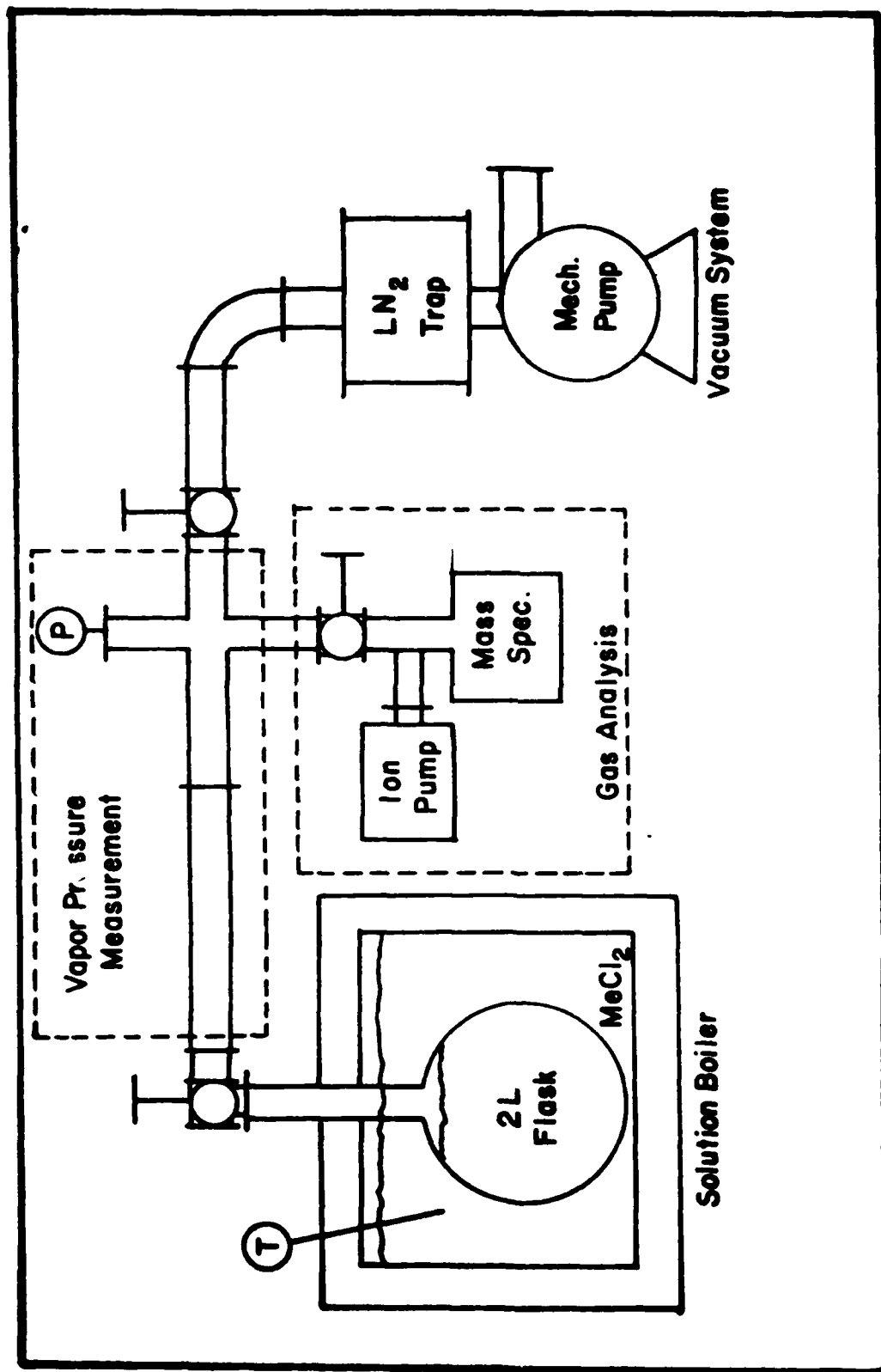


FIGURE 1
Schematic of Experimental Apparatus

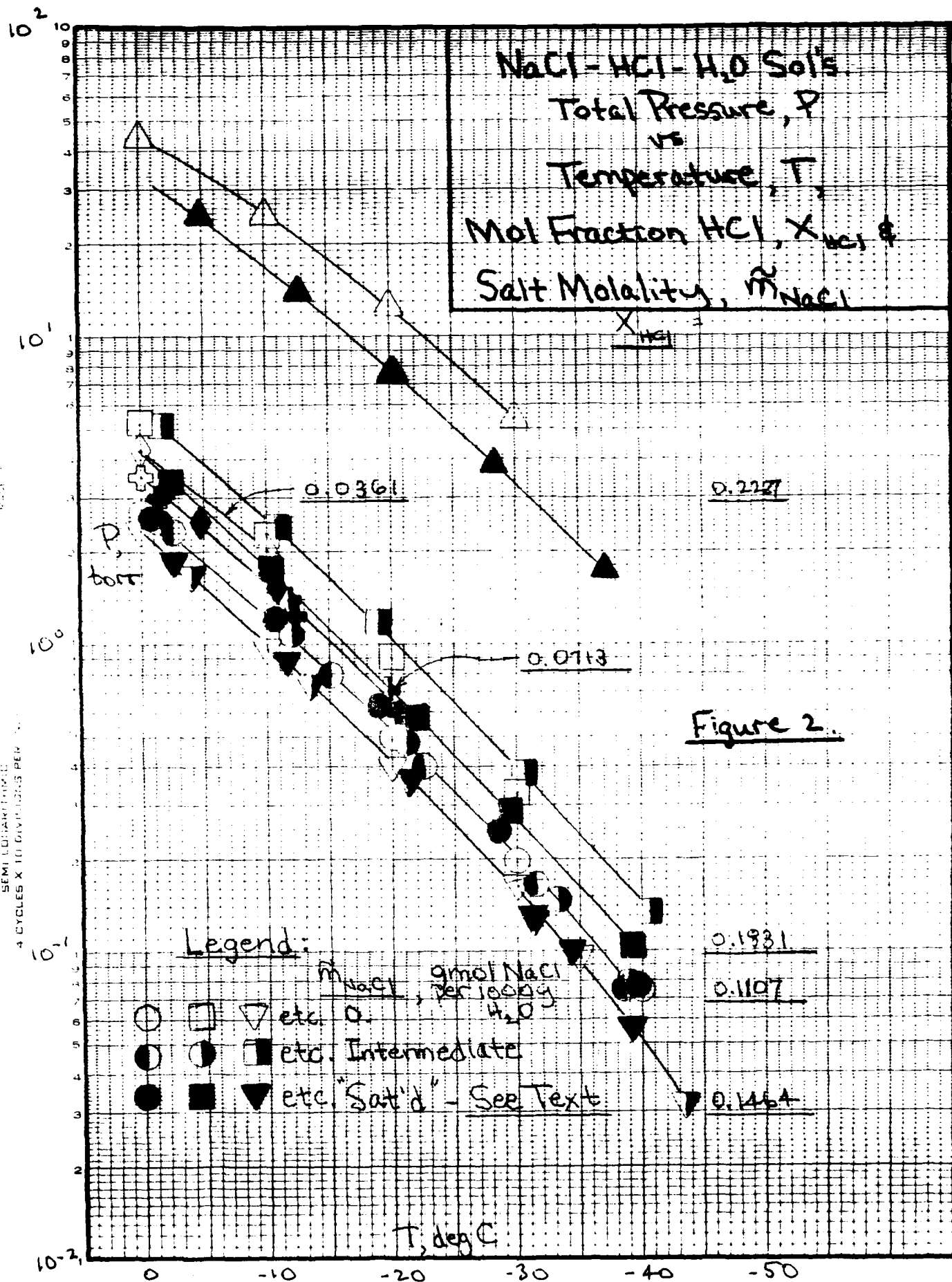
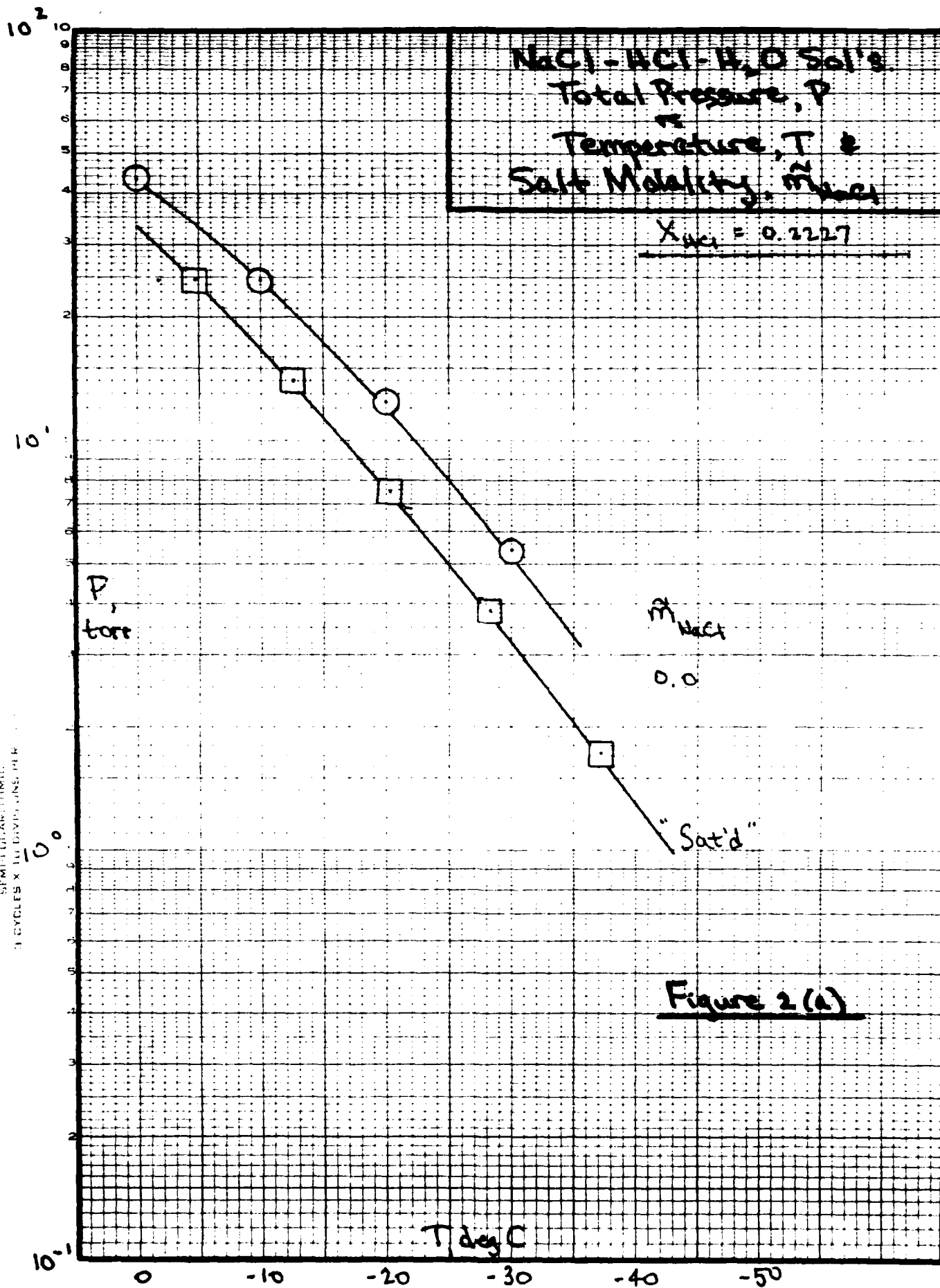


Figure 2.



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P,
torr

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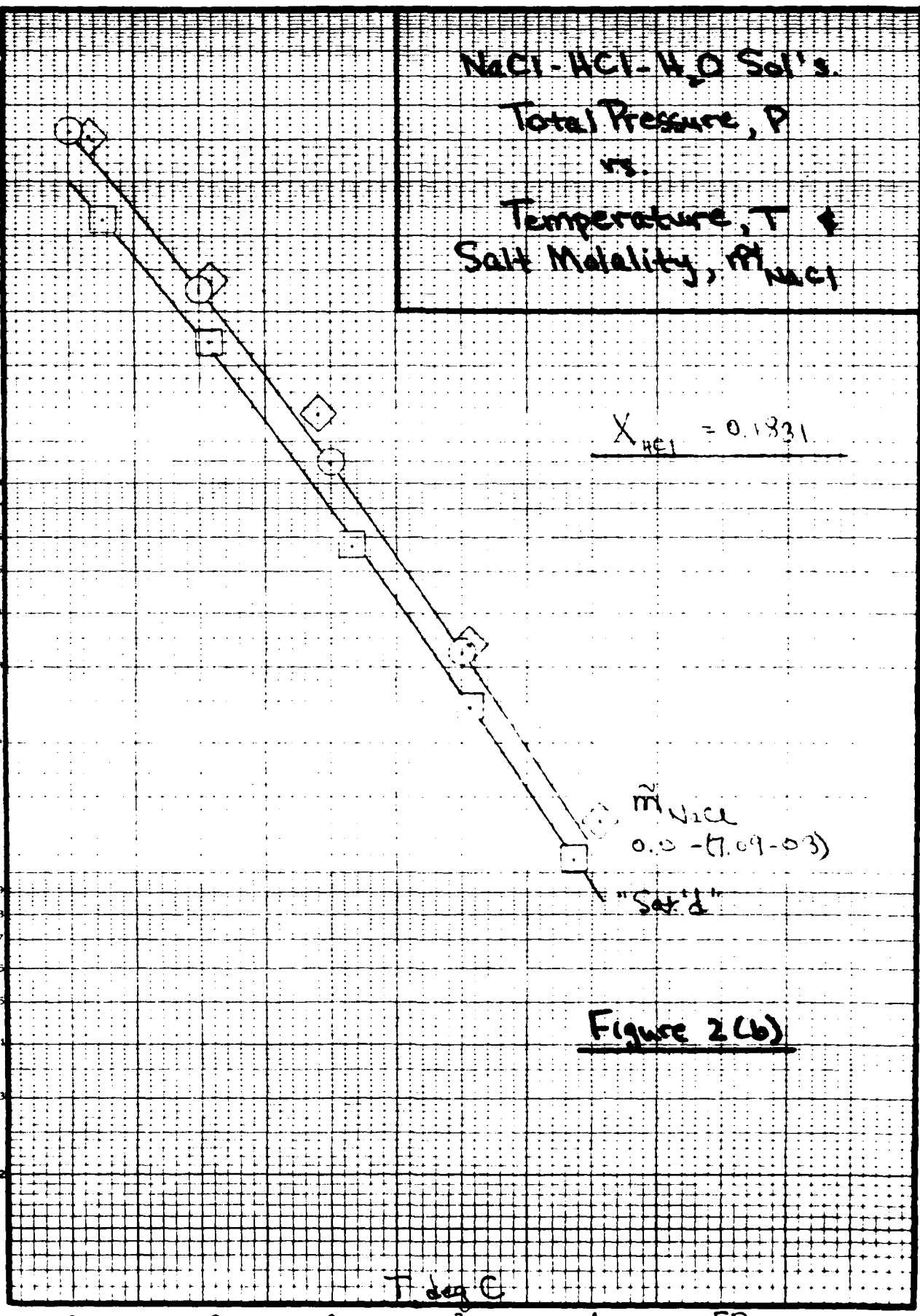
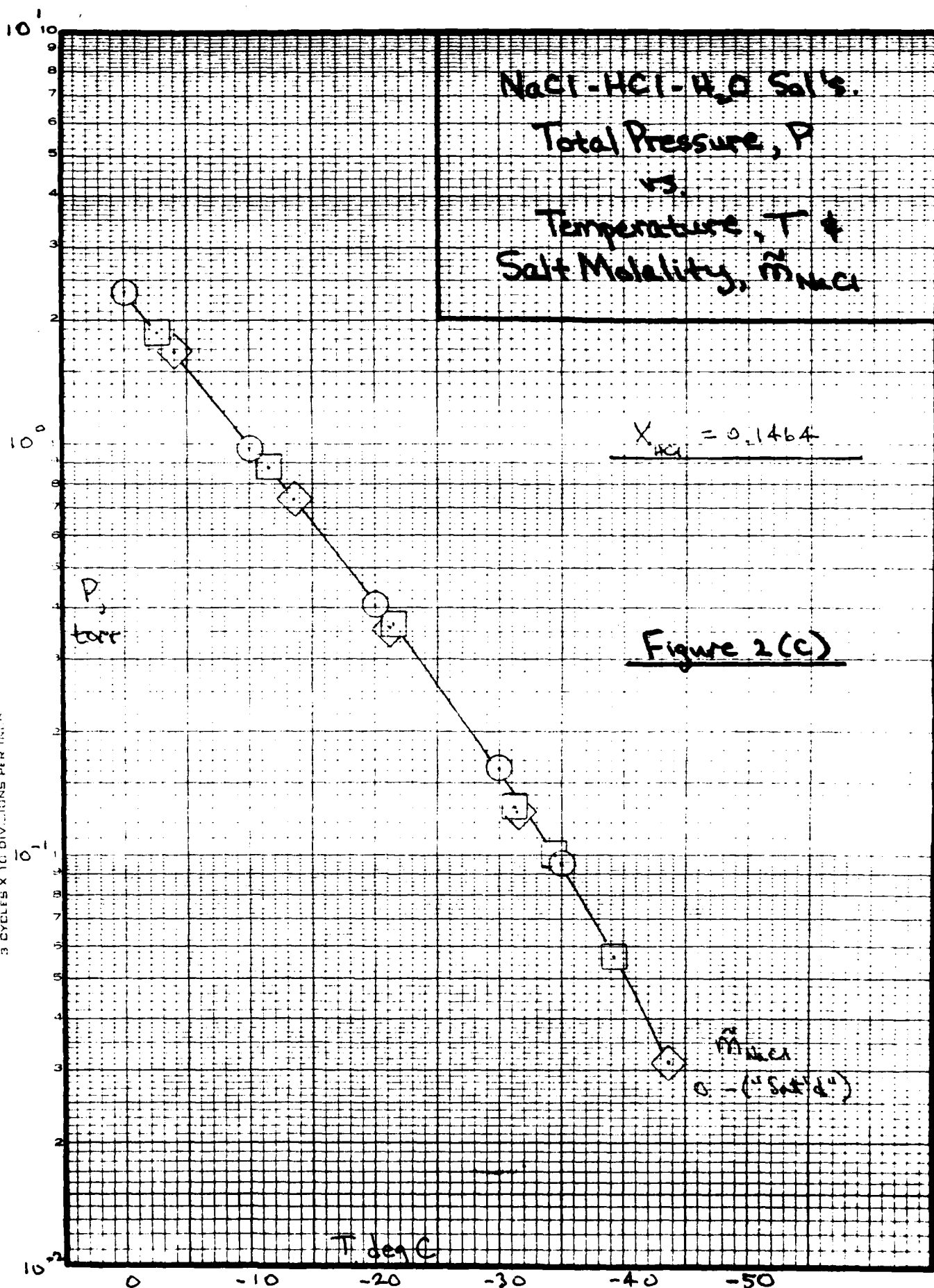


Figure 2(b)



NaCl-HCl-H₂O Sol's.
Total Pressure, P
vs.
Temperature, T
Salt Molality, \bar{m}_{NaCl}

$$X_{NaCl} = 0.1107$$

P,
torr

\bar{m}_{NaCl}
o - "Sat'd"

Figure 2(d)

T, deg C

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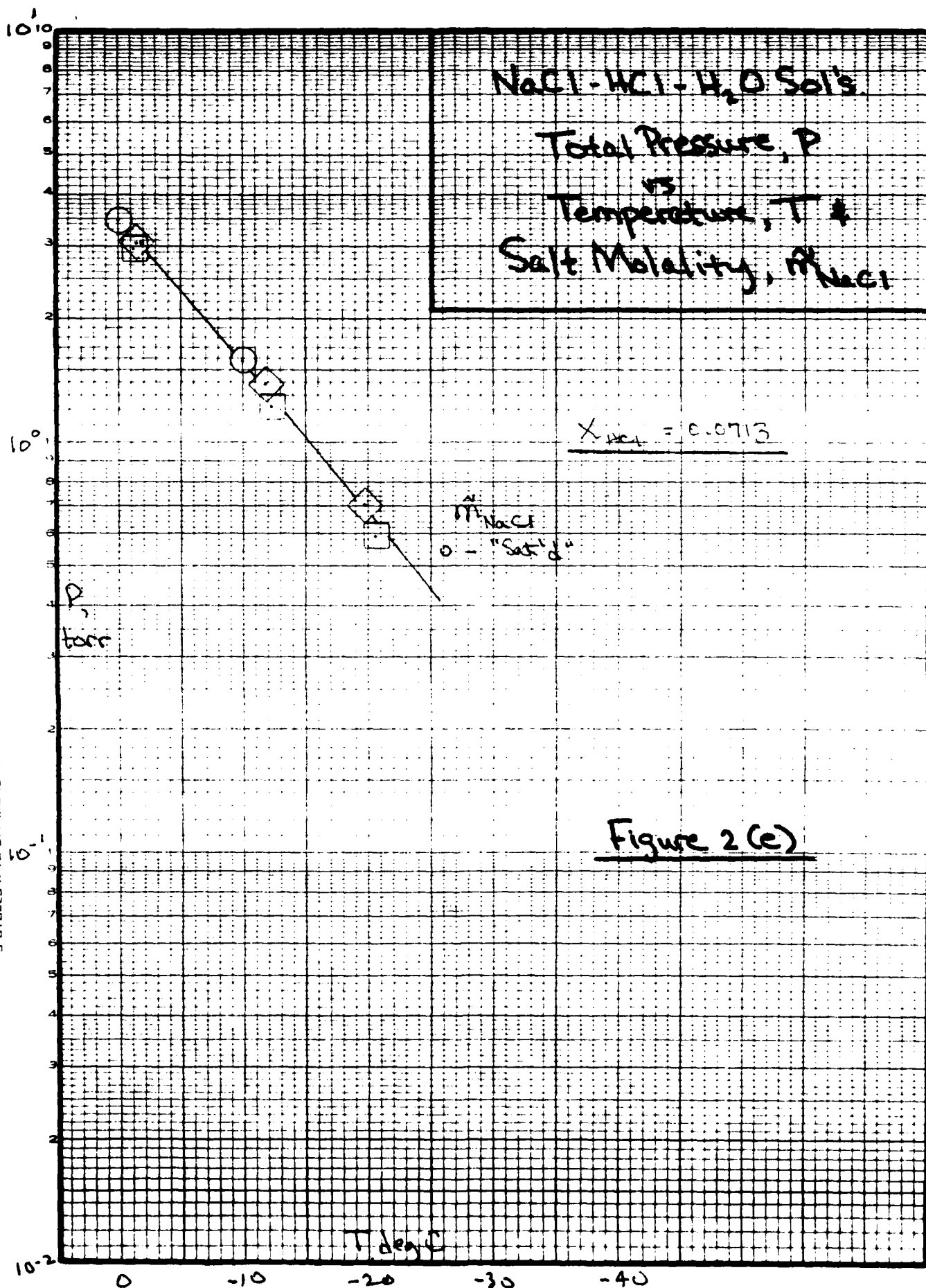


Figure 2(c)

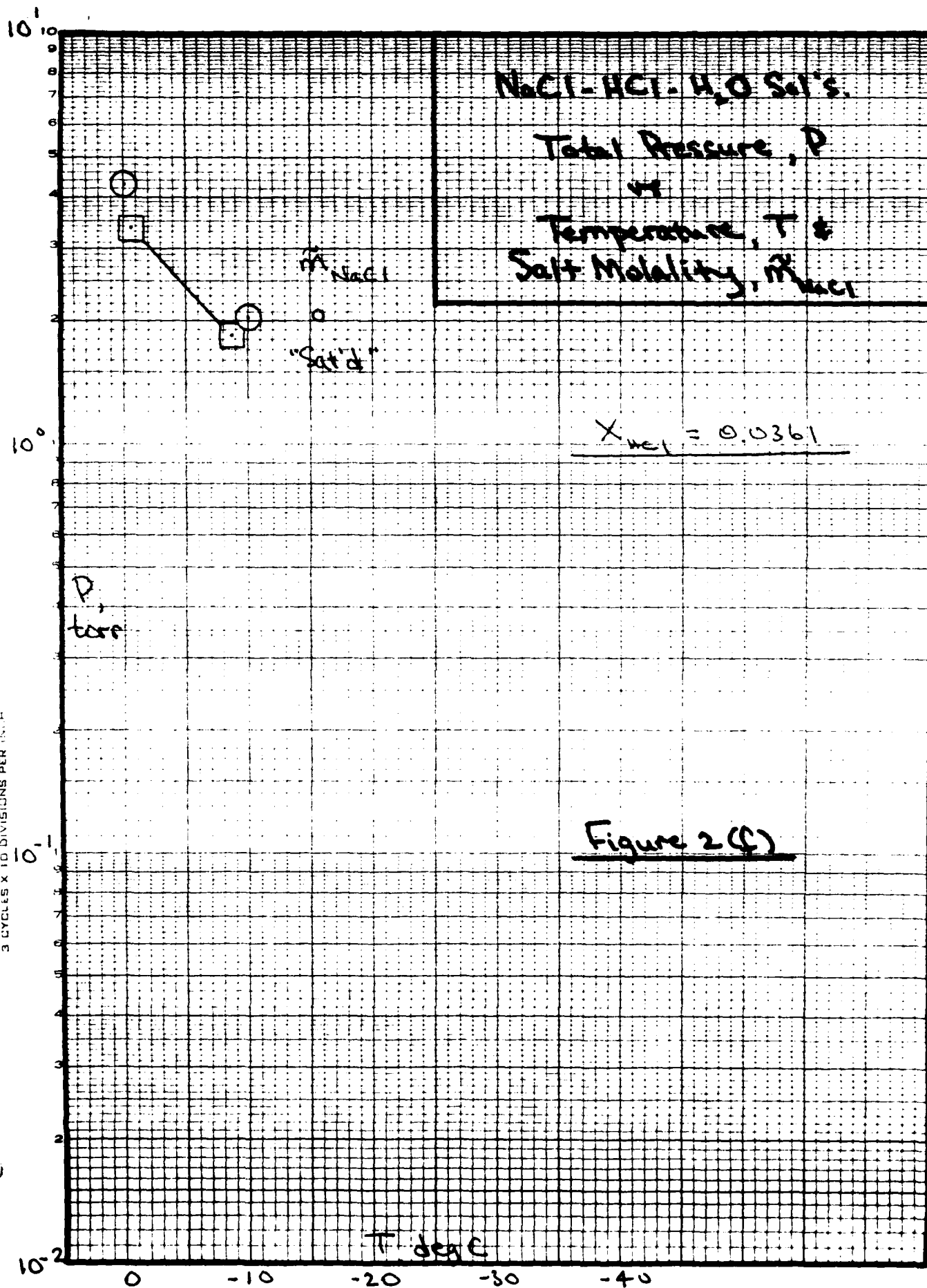
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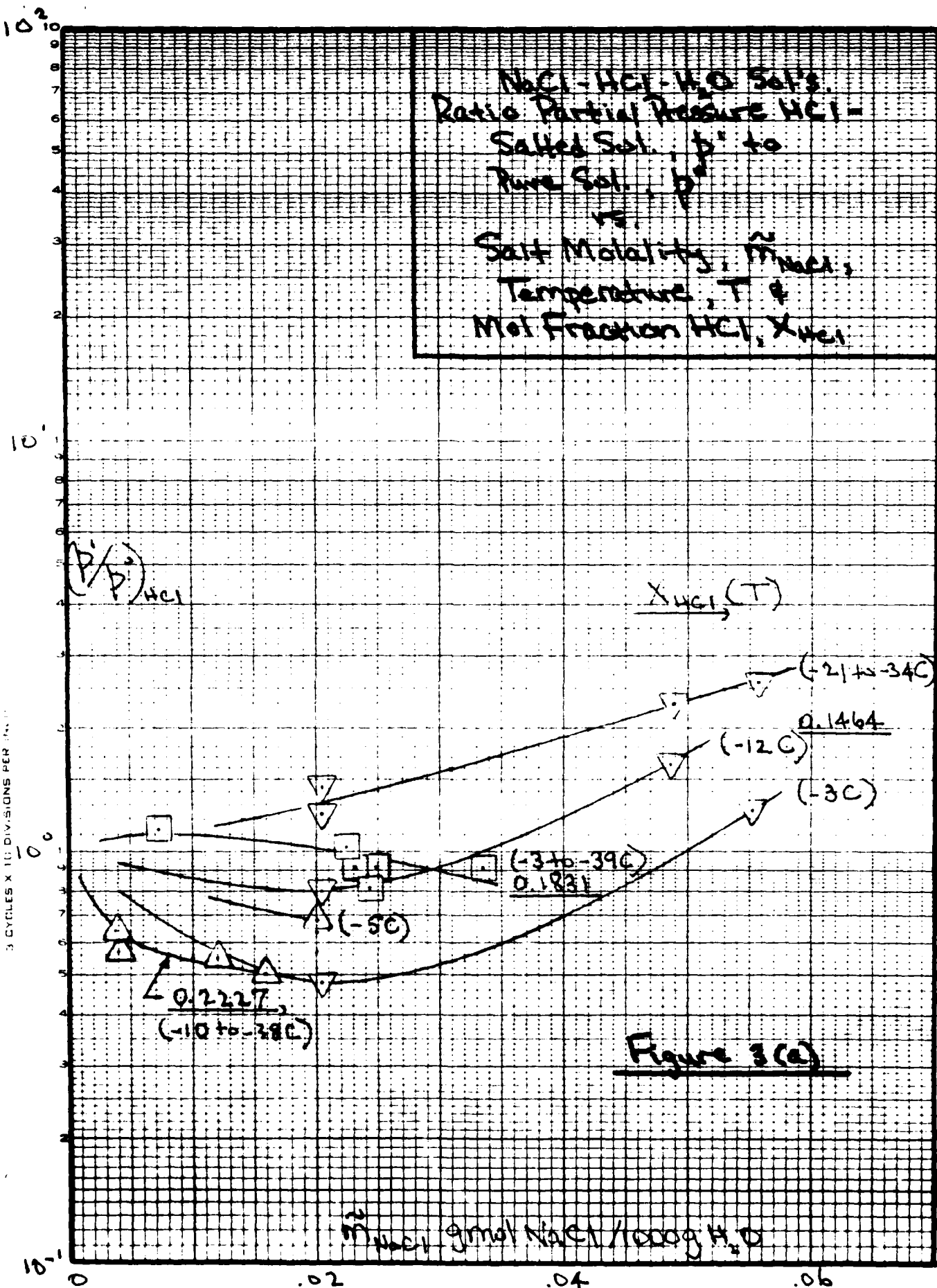
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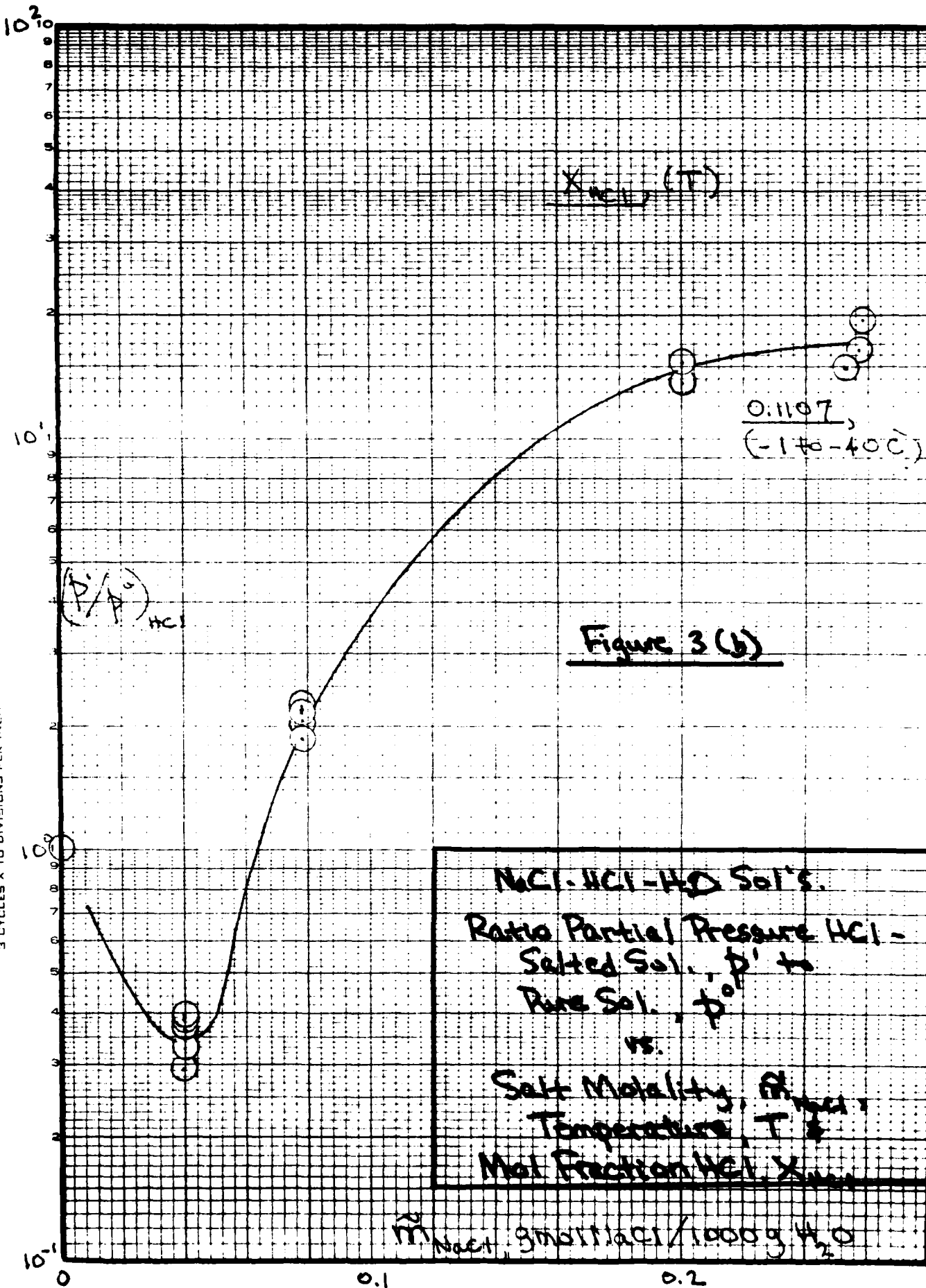
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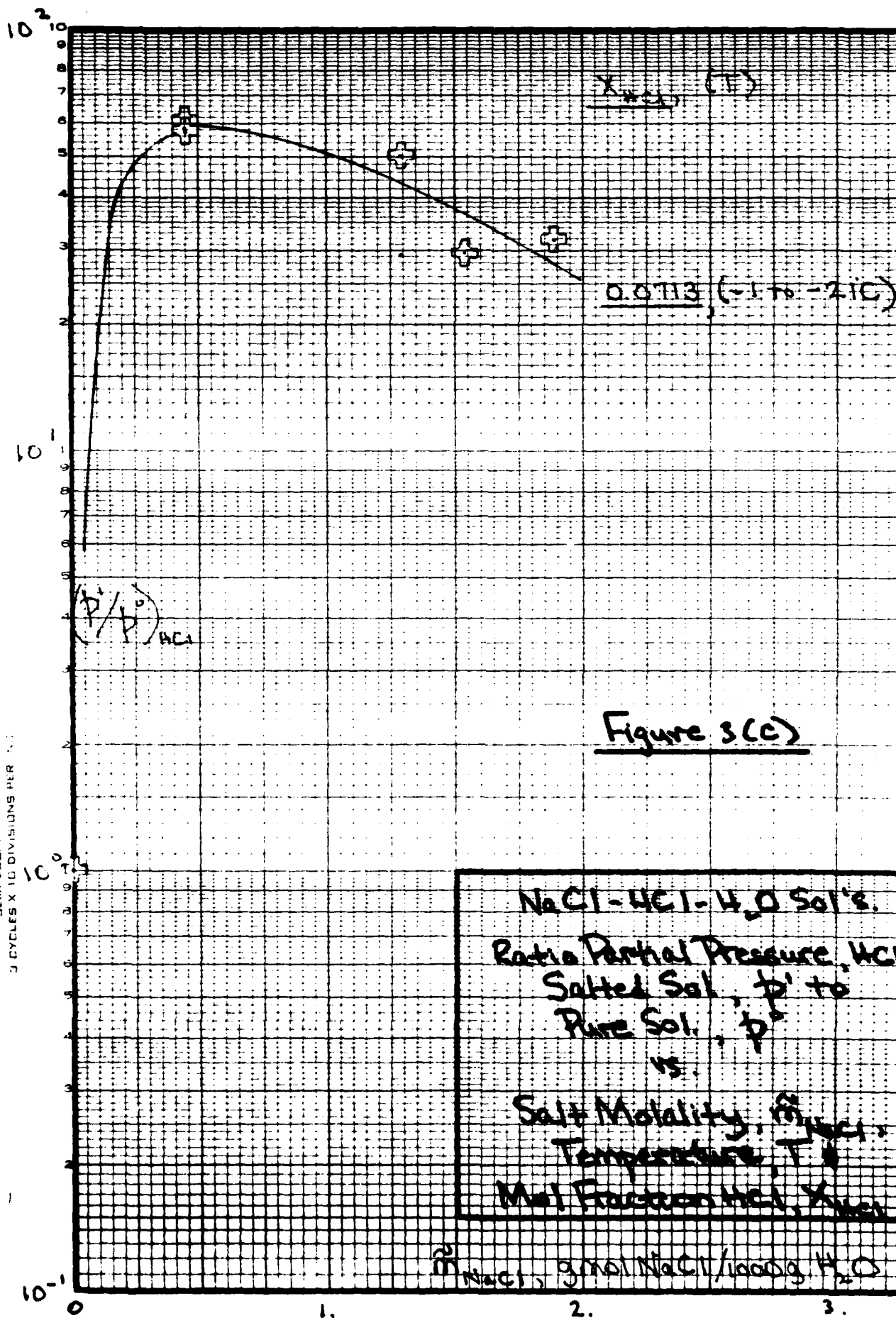
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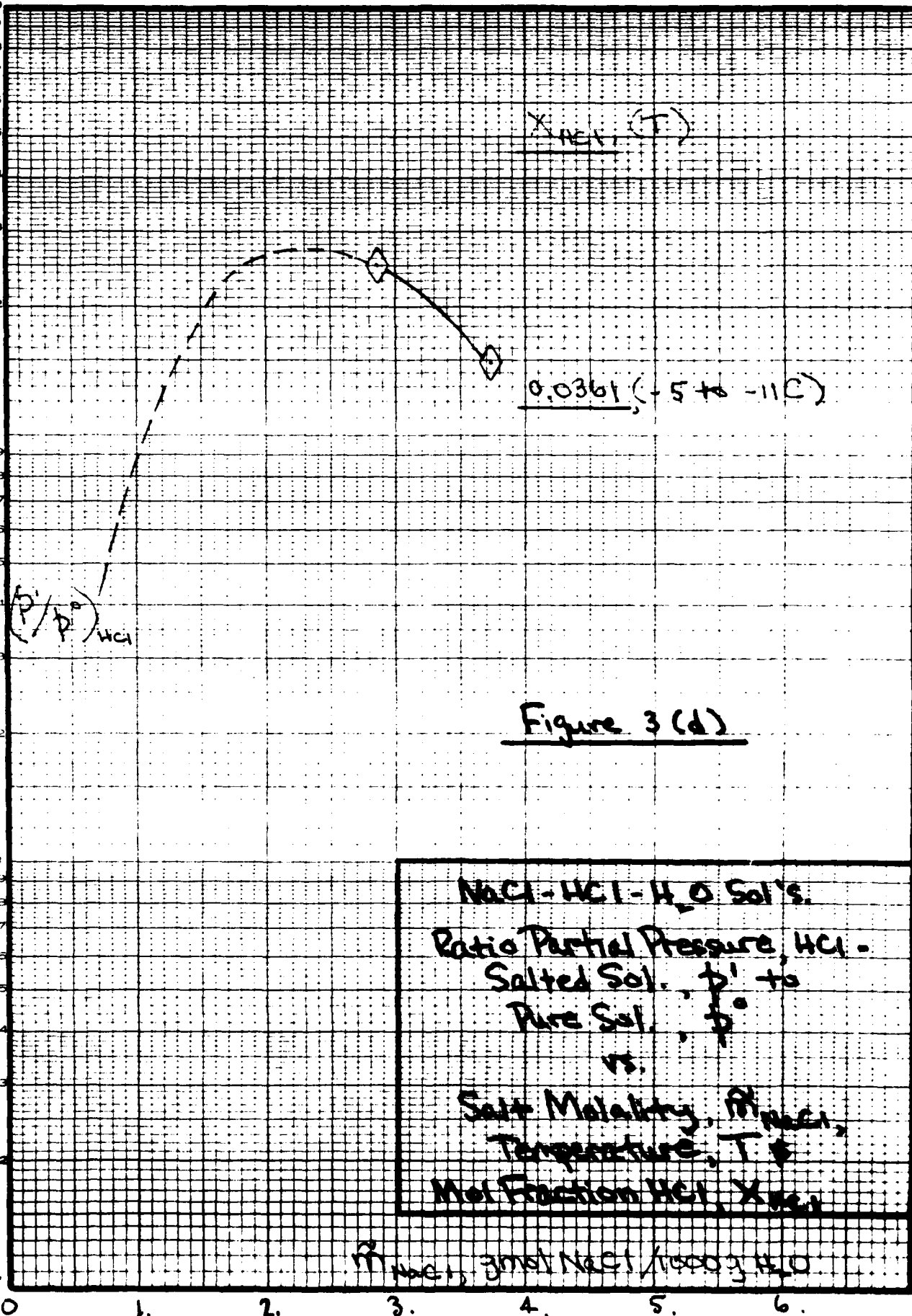
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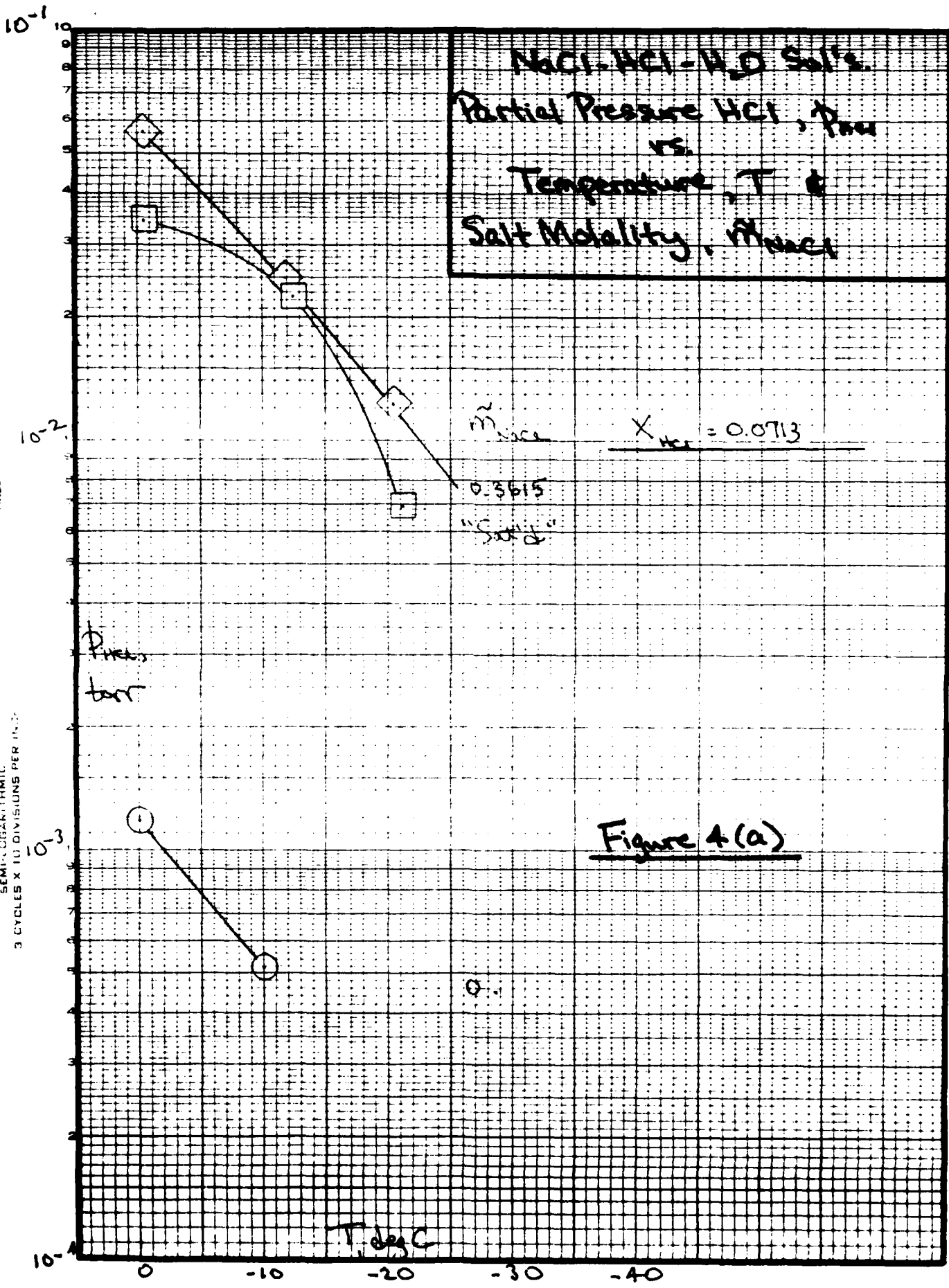
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10⁵
10⁴
10³
10²



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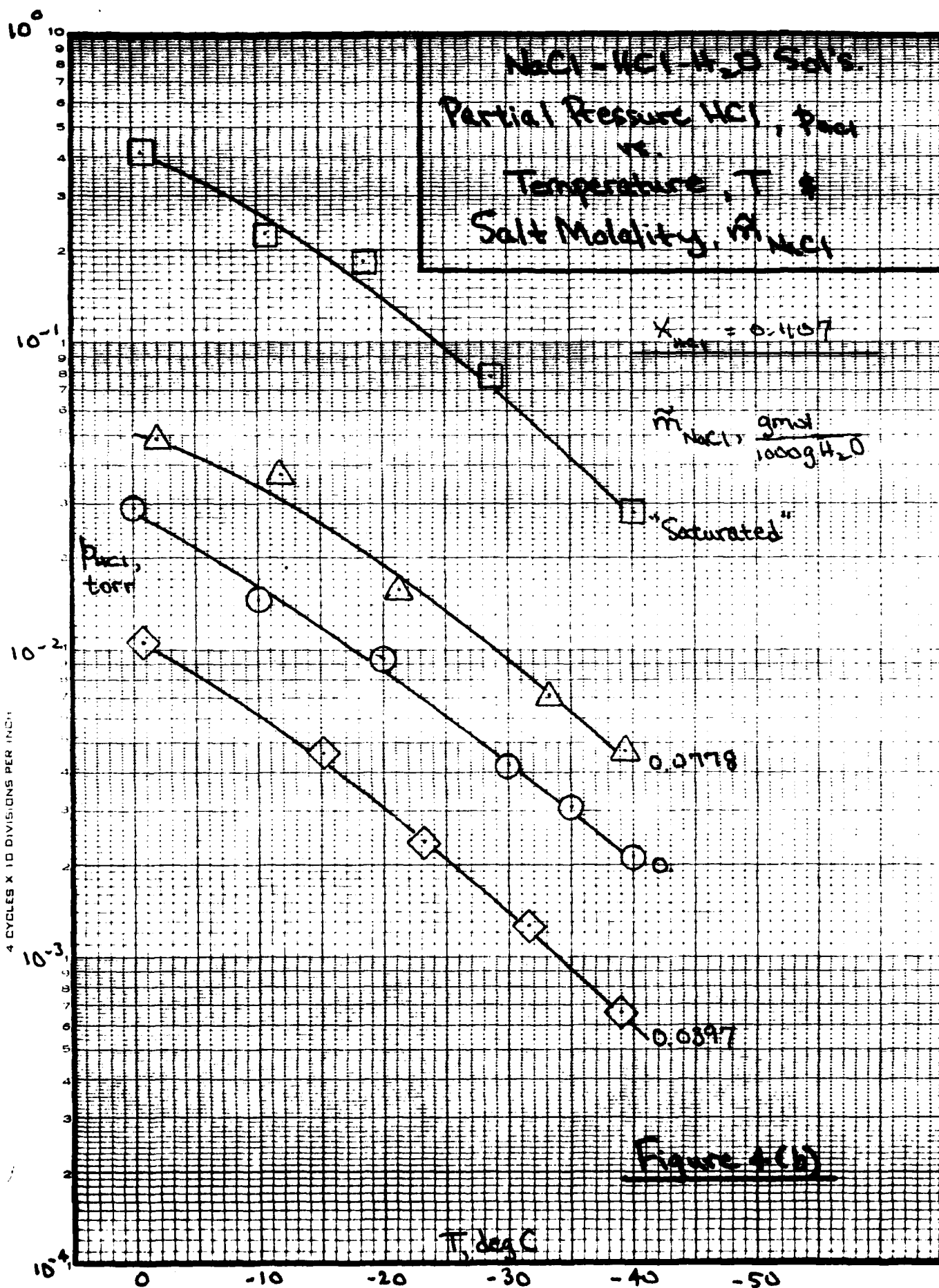


Figure 4(b)

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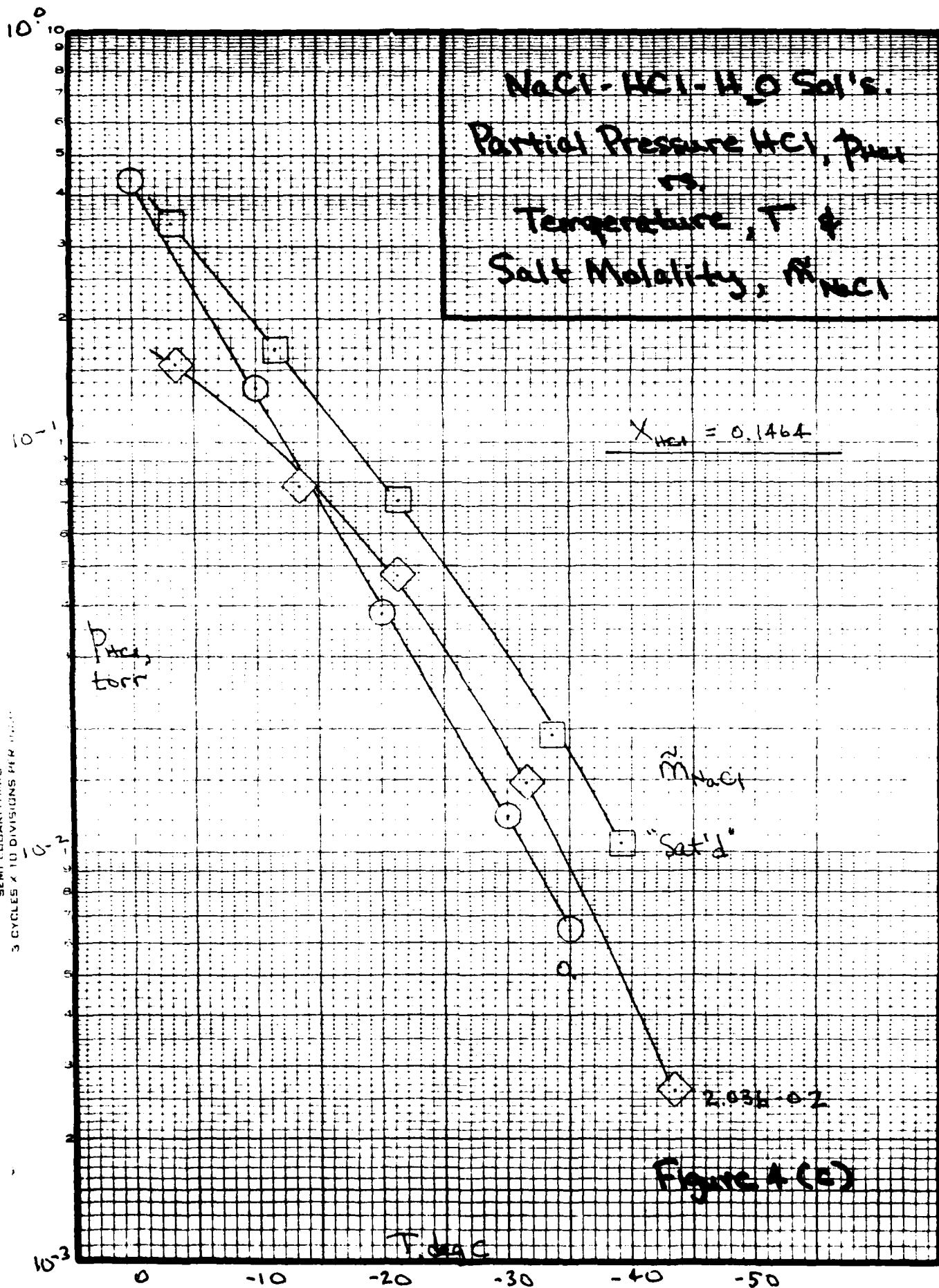


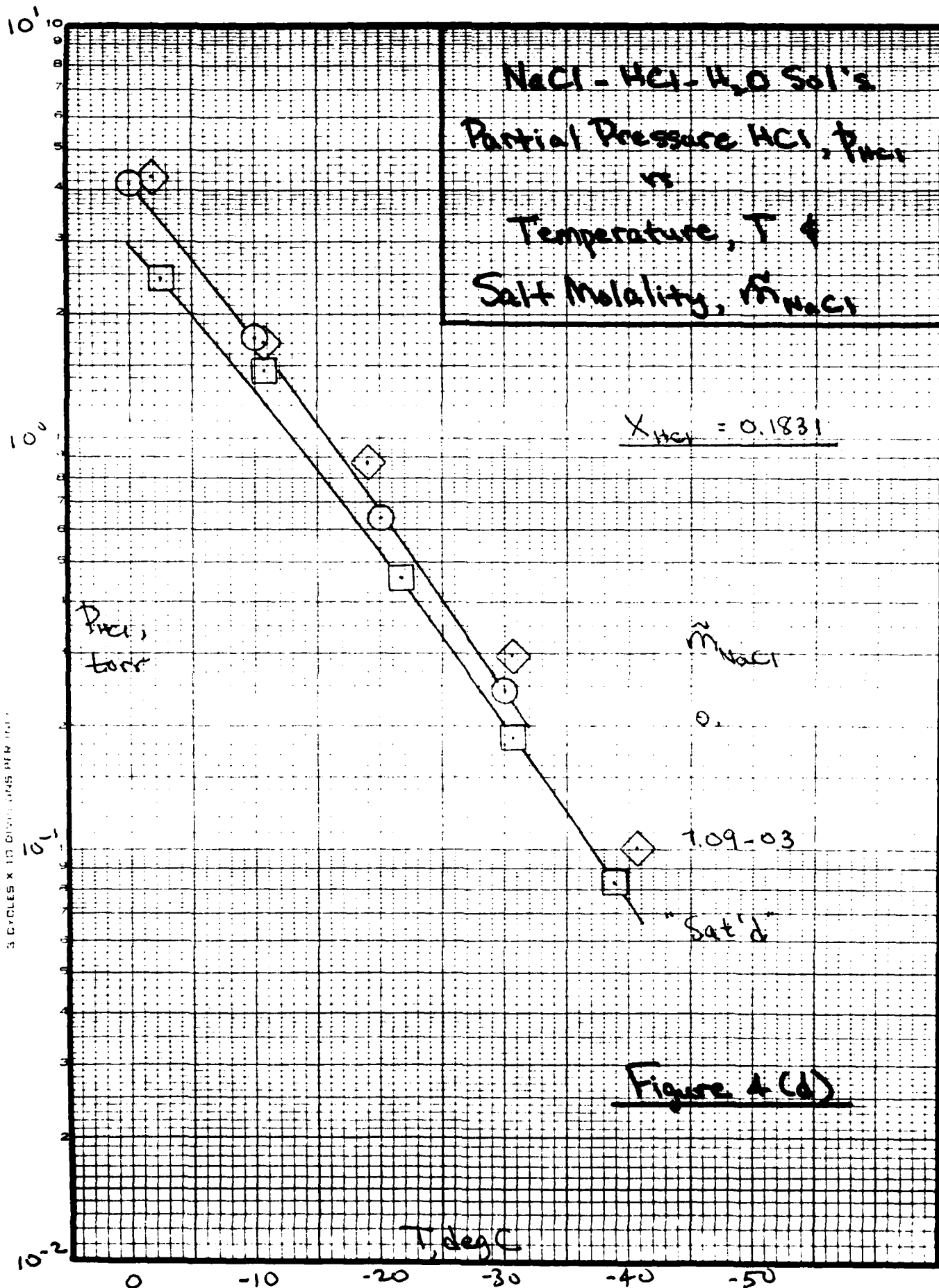
Figure 4(c)

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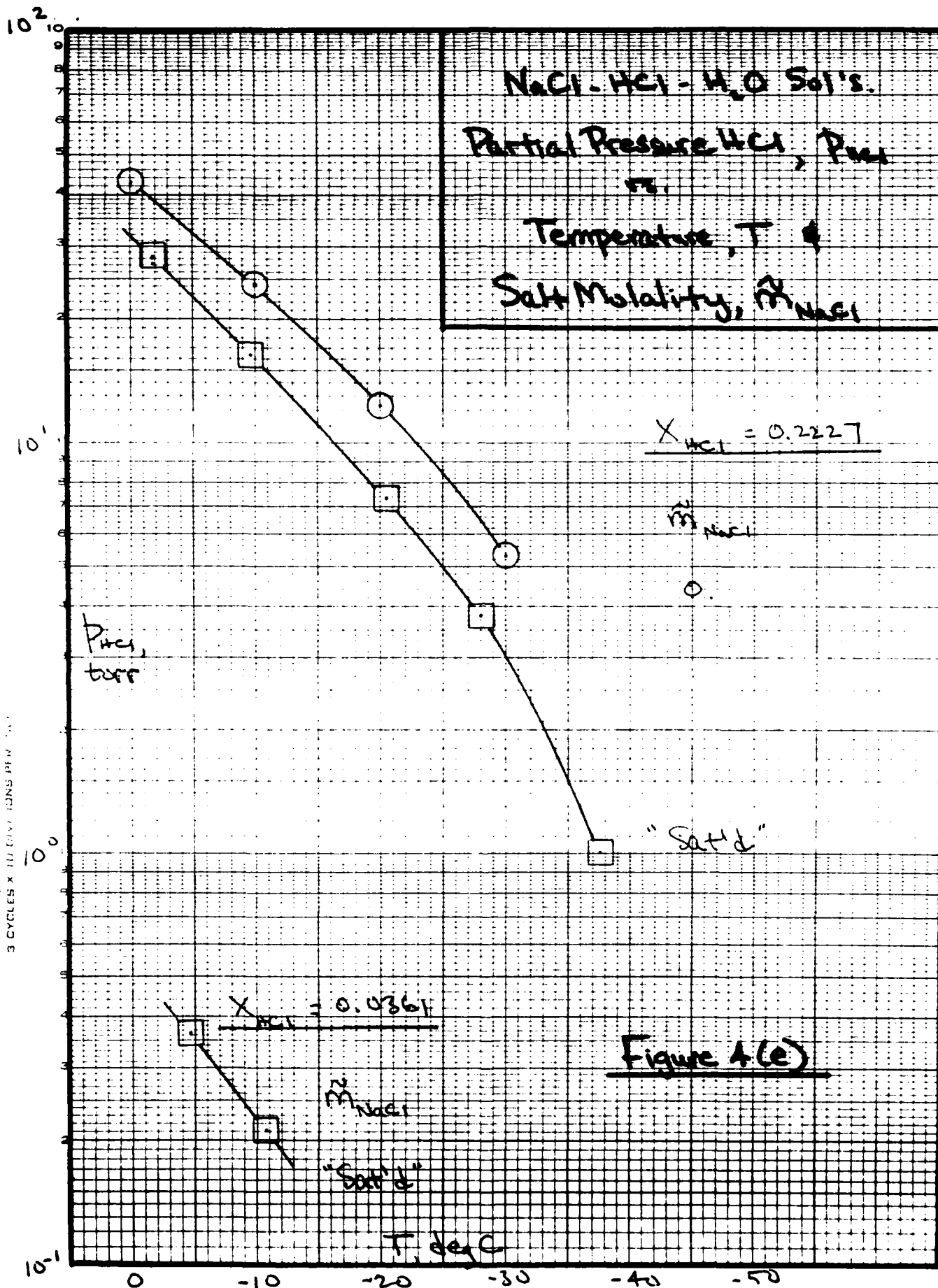


Figure 4(e)

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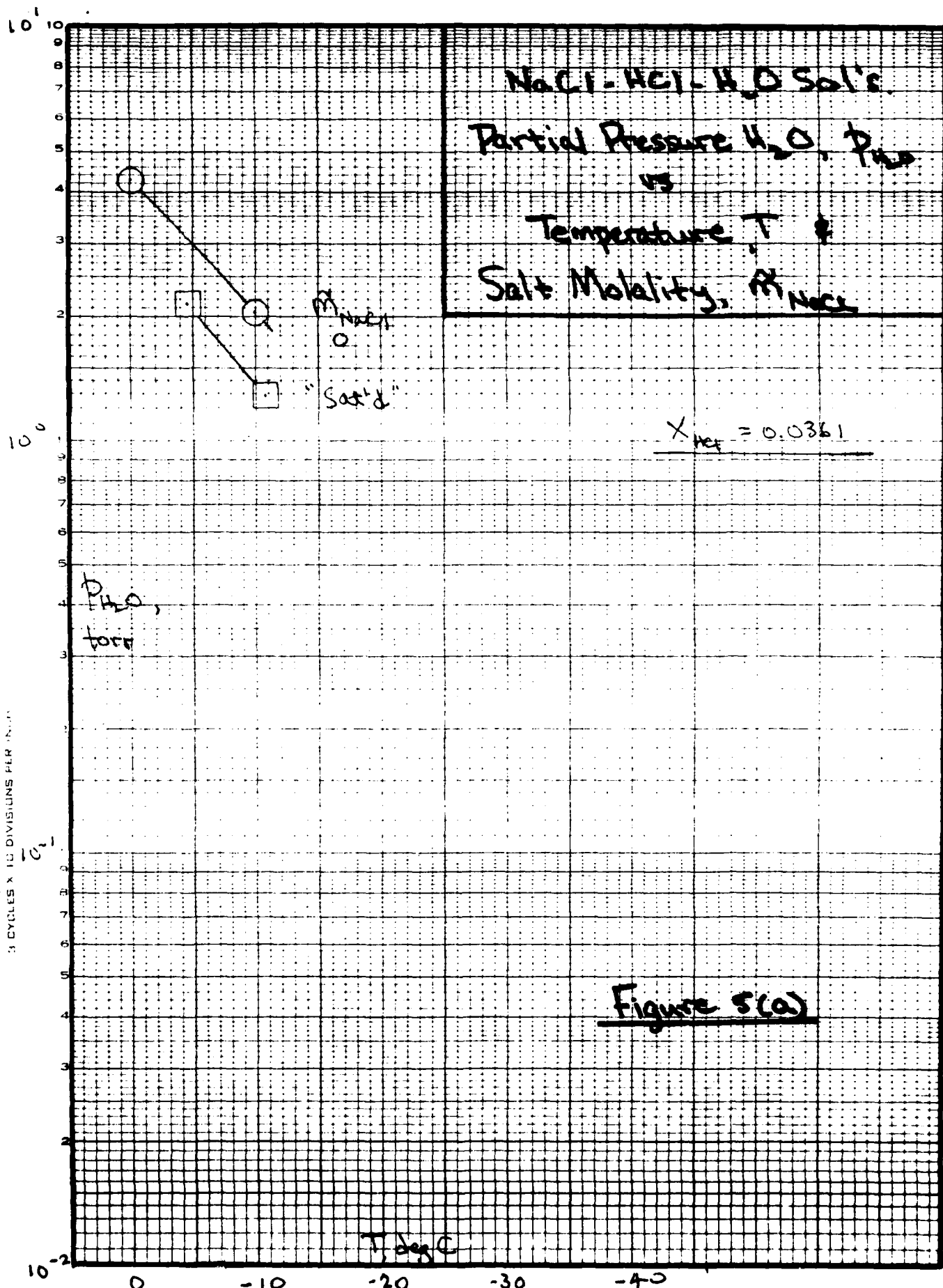


Figure 5(a)

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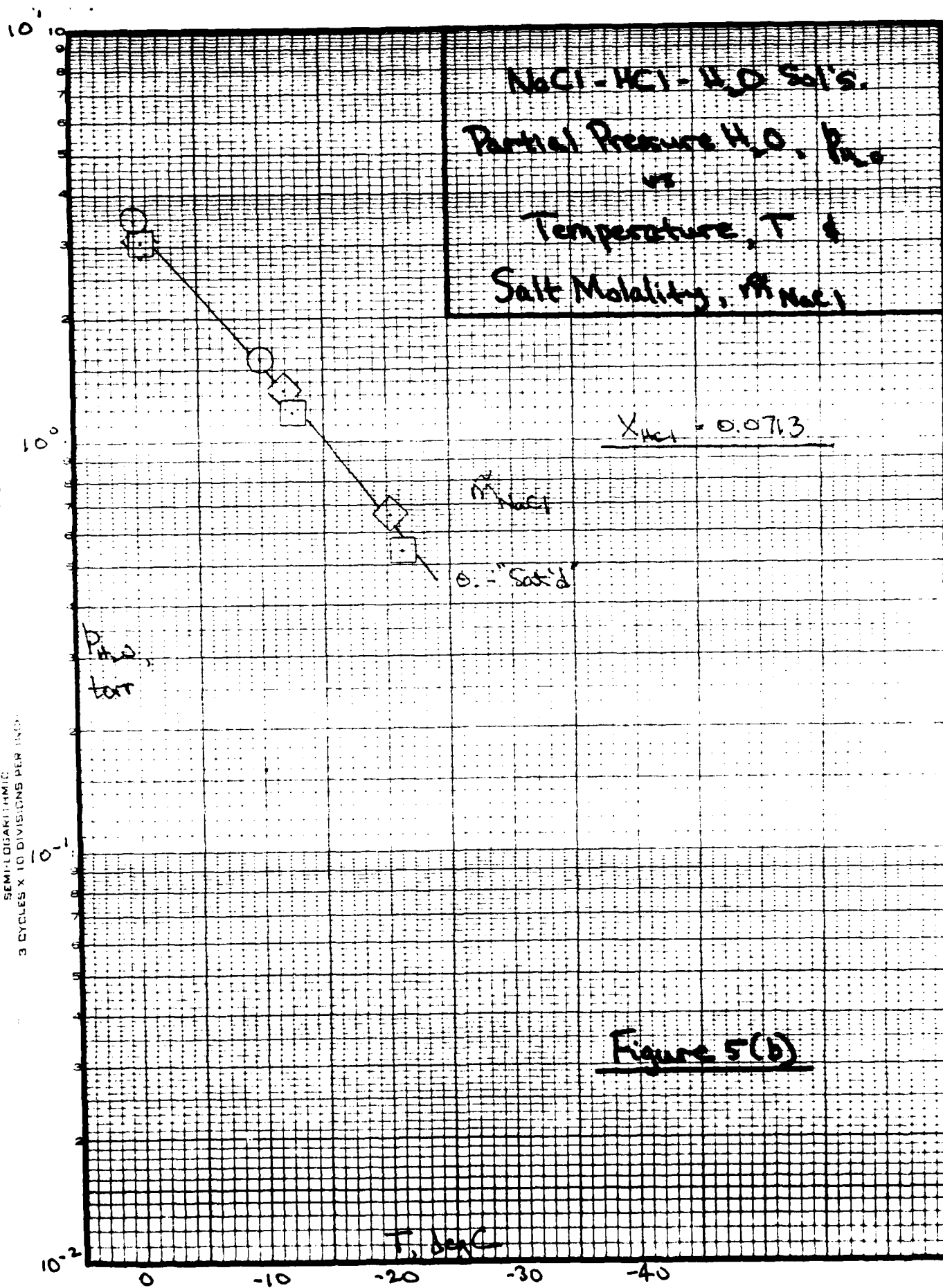
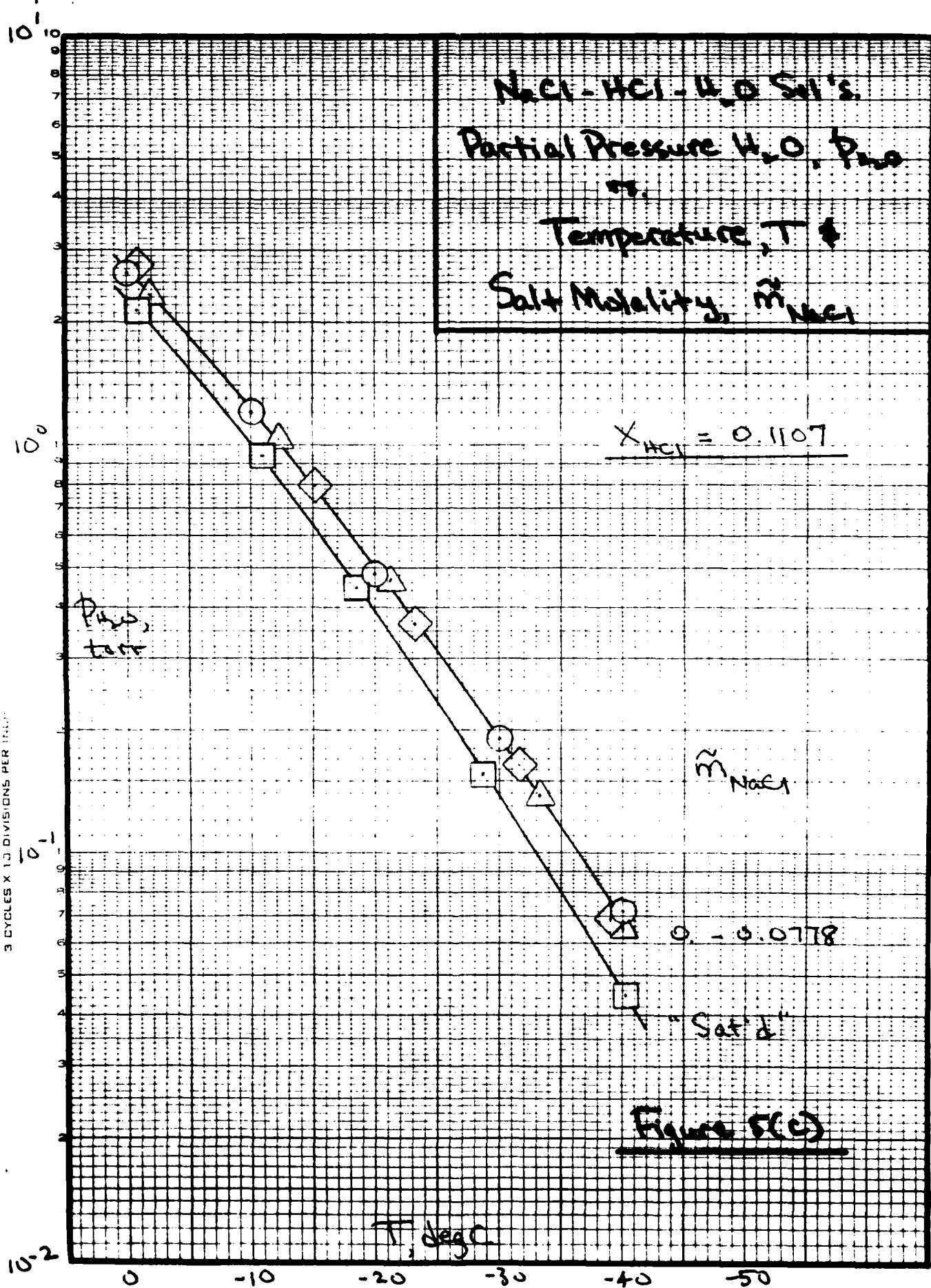


Figure 5(b)

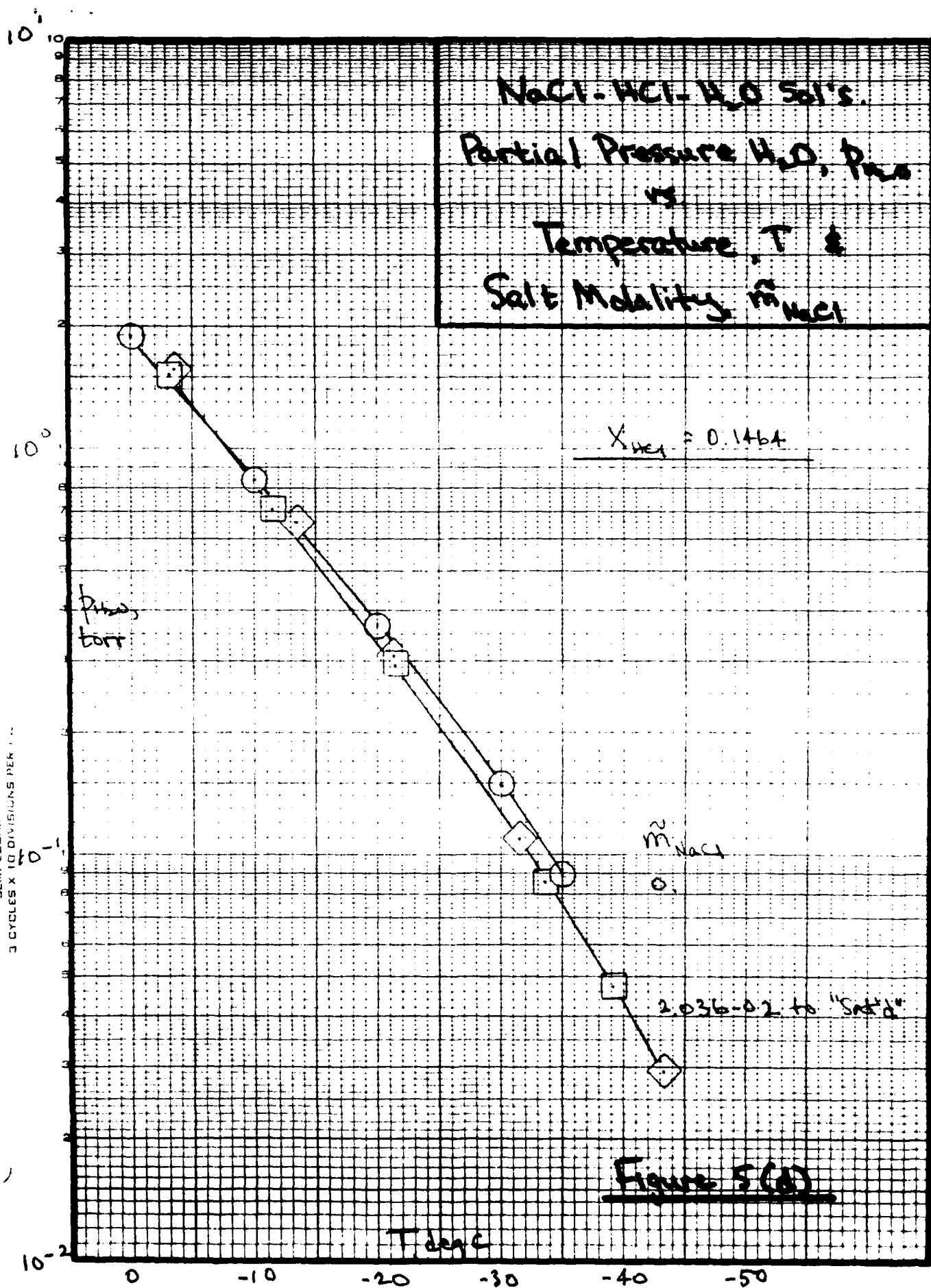
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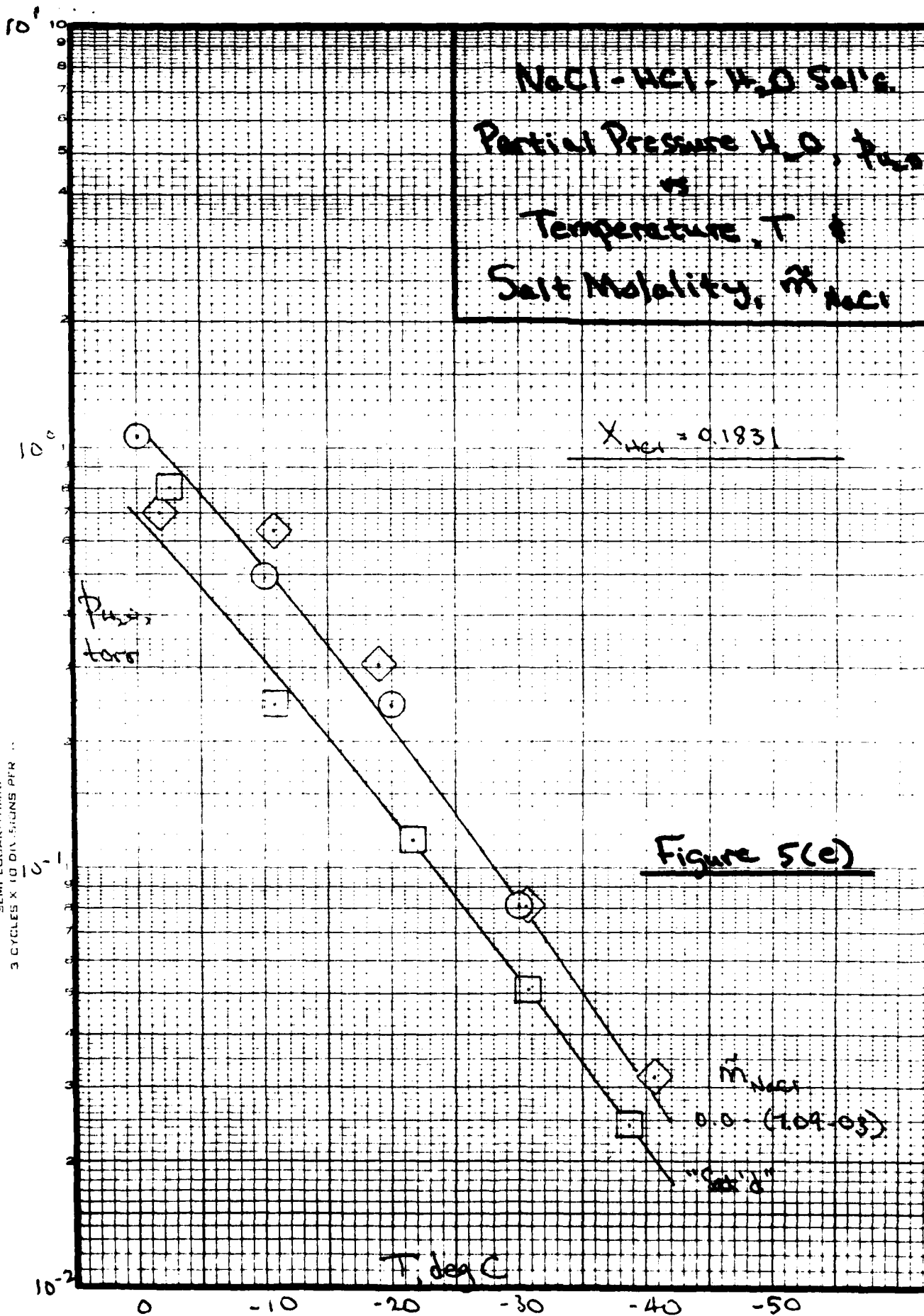


Figure 5(c)

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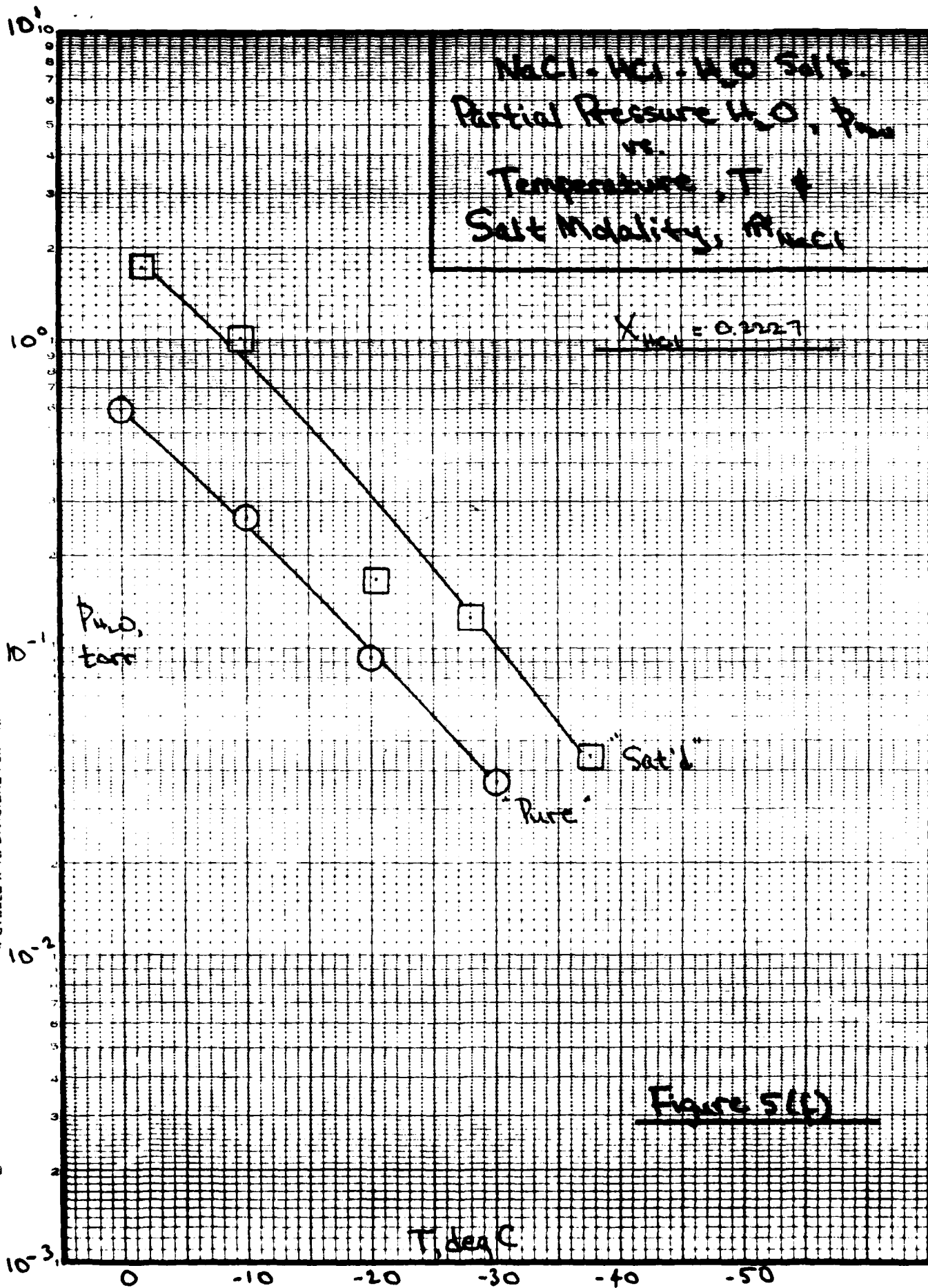


Figure 5(1)